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ELECTRONIC STRUCTURE, BONDING, AND CHEMISORPTION IN METALLIC HYDRIDES

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ABSTRACT

Problems that can arise during the cycling steps for a hydride storage system usually involve events at surfaces. Chemisorption and reaction processes can be affected by small amounts of contaminants that may act as catalytic poisons. The nature of the poisoning process can vary greatly for the different metals and alloys that form hydrides. A unifying concept is offered, which satisfactorily correlates many of the properties of transition-metal, rare-earth and actinide hydrides. The metallic hydrides can be differentiated on the basis of electronegativity, metallic radius (valence) and electronic structure. For those systems where there are d (transition metals) or f (early actinides) electrons near the Fermi level a broad range of chemical and catalytic behaviors are found, depending on bandwidth and energy. The more electropositive metals (rare-earths, actinides, transition metals with $d < 5$) tend to strongly chemisorb electrophilic molecules; this is a consequence of the manner in which new bonding states are introduced. More electronegative metals ($d \geq 5$) dissolve hydrogen and form hydrides by an electronically somewhat different process, and as a class tend to adsorb electrophobic molecules. The net charge-transfer in either situation is subtle; however, the small differences are responsible for many of the observed structural, chemical and catalytic properties in these hydride systems.

INTRODUCTION

Interest in hydrogen energy storage systems has spread quickly worldwide. A broad-base, high-diversified scientific effort has gone almost hand-in-hand with the work on engineering and hardware--an unusual and fortunate state. The ultimate reliability of a hydride storage system will depend upon reproducibility in cycling. It is well-known that the chemisorption and reaction steps can be affected by small amounts of contaminants that act as catalytic poisons; furthermore, the nature of the poisoning process can vary greatly for the different metals and alloys that form hydrides.

A great deal is already known about acid-base catalysis [1], and specific catalytic poisons have been studied extensively, particularly in metal oxide catalysis [2]. For metal/metal hydride systems much less is known, partly because hydride surfaces are difficult to characterize, and the electronic structure and bonding in these materials has only recently begun to be better understood. A unifying concept is offered here, which satisfactorily correlates many of the properties of transition metal, rare earth and actinide systems. These as a class form metallic hydrides; they and their alloys are basically the materials of interest in energy storage research. The correlation presented here is largely empirical, intended to draw together a number of diverse observations, and perhaps stimulate some thought into new avenues of research.

General Observations

1. Metallic hydrides are at least trivalent. Close metal-metal spacing is required in order to have orbital overlap. The entering hydrogen should be considered as metallic, as any other metallic alloy addition.
2. Most of the catalytic properties of the transition metal and rare earth hydride systems are describable in terms of d-electron

interactions.

3. Most of the properties of the actinide systems (through Pu) are describable in terms of f-electron interactions.
4. If the d's (or f's) are involved in metallic bonding, they will not in general be easily available for chemisorption/catalysis. Conversely, if they are not involved in bonding, they will be--depending on energy, degree of localization and certain structure factors--available for chemisorption.

Specific observations within this framework

1. Highly electropositive metals--actinides, rare earths, early transition metals--form hydrides with the addition of new, hydrogen-derived states below the Fermi level, to which metal electrons are attracted. Characteristic properties of these systems are as follows:
 - a. In terms of electronegativities the $\Delta n = (H - M)$ value is in the range 0.5-1.0 (see Fig. 1).
 - b. The heats of reaction and solution are exothermic.
 - c. The hydrogens are found in tetrahedral positions.
 - d. The hydriding reaction tends to be poisoned by electrophilic molecules.
2. Less electropositive metals--e.g. Fe, Co, Ru, W...
 - a. Have high valencies, large cohesive energies, and resultant lattices too small to easily form hydrides.
 - b. Exhibit a Δn in the range 0.5-0.2.
 - c. The heats of solution become endothermic.
 - d. May cause major electronic effects as alloy additions.
3. Still less electropositive metals--e.g., Ni, Pd,...
 - a. Form hydrides both by adding electrons to nearly-filled

metal d-states and also new states drawn below the Fermi level, in complex manner.

- b. Exhibit a Δn in the range 0.1-(-0.1).
- c. Show complex heats of solution/reaction.
- d. The hydrogens are found in octahedral positions.
- e. The hydriding reactions tend to be poisoned by electrophobic molecules.

DISCUSSION

The pioneering band-structure work by Switendick [3-6] has given impetus to a large number of new solid-state efforts, coupled with studies by various surface-sensitive spectroscopies. The old "protonic" and "anionic" models have all but vanished with this new understanding, though there is still much controversy over details and a full comprehension is no doubt some time away. The enormous complexities of heterogeneous catalysis cannot be addressed here in any detail, but a number of observations can be made that appear to be consistent for various metals and classes of metals.

The surface

For a metal/metal hydride system we may also be dealing with various kinds of oxide and/or hydroxide layers which will certainly be present under most normal conditions, and will strongly affect UHV measurements. Such layers, as well as certain impurities and inclusions, may completely alter the observed chemistry. Bulk properties must also be considered, and diffusion processes become involved in later stages of hydriding. In catalytic processes the concept of active sites due to disorder or substoichiometry is important; for example, the catalytic activity of the rare earth oxides is perhaps better explained by substoichiometry than by a model based on paramagnetic centers [7].

Though a surface may be predominantly basic, as would be expected for an electropositive metal, the rare earth oxides, etc., there may still be many other active centers due to defects, dislocations, inclusions, acid-base pairs, etc. An excellent discussion of the electronic theory of catalysis has been given by Vol'kenshtein [8].

Types of poisons

When we speak of electrophilic (electron-seeking or electron-deficient) molecules we are considering chemisorption upon potentially electron excess surfaces; examples include the electropositive metals, and particularly p-type semiconductors. A large number of gaseous molecules could be listed that might occur as atmospheric contaminants: SO_2 , CO_2 , HCl , O_2 , various organic molecules with acidic character, etc. CO occupies an intermediate position due to its unique electronic structure. Water is considered amphoteric, acting either as an acid or base, as well as possible becoming an oxide, hydroxide or even hydride former under certain conditions. Electrophobic (electron-donating) molecules include such obvious examples as NH_3 , other amines, pyridine, etc.

Now these molecules interact in detail has been the subject of many papers, for example the huge literature on the adsorption of CO on transition metals. What is of immediate interest is the fact that the interaction is electronic--the poison simply can tie up the surface states normally used for hydriding. In this regard we should invoke the Labatier-Balandin "volcano relationship" [9,10] which says simply that if a reactant is too strongly adsorbed it is ineffective (e.g., oxygen chemisorption usually leads to oxidation), and also it will not be present in active form if too weakly adsorbed.

Methods of interpretation

In describing the hydriding process the physical chemist may think in terms of heats of formation, hydrogen fugacities and activation energies. Engel-Brewer theory will suggest configurations produced by s, p, and d electrons and the promotion energies necessary to minimize the total energy [11]. From the structure viewpoint, many of the properties of hydrides can be described in terms of minimum bond lengths, which in turn dictate at least in part the structures and phase diagrams. Finally the theorist and solid-state physicist will speak about band-filling, Fermi energies and densities of states. All these different languages can describe the same process. Each gives a special viewpoint which contributes to the whole. In the discussion of the metal systems below, the various languages will be used freely.

As a basis for comparison, a plot of electronegativities is shown in Fig. 1. The highly electropositive mono- and divalent-metals form salts and will not be a part of this discussion. The rare earths, Sc, Y are aggressive hydride formers; Ti, Zr, Hf, somewhat less so, etc. Circled metals do not form hydrides, the ones in parenthesis can be forced into (unstable) hydriding configurations by drastic methods such as electrolytic charging. The difference between hydrogen and a particular metal ($=\Delta n$) may be viewed as a driving force or potential for reaction. For the Group VIII metals this actually appears to become negative, signalling perhaps a different kind of hydriding process. For each of the metal systems the electronic properties and the related effects of adsorbing gases will be outlined.

Rare-earths

The highly-electropositive rare earths will be considered first; much can then be applied to the transition metals and actinides. Chapter 9

of "Metal Hydrides" [12] provides a broad review of rare earth hydride properties.

The valence band structure of a typical rare earth is thought to consist of a nearly-filled s-band and a d-band population varying from about one to more than two electrons [13]. The 4f's quickly become localized into magnetic, atomic-like states. Even in Ce the γ -phase exhibits a normal moment, though under high pressures the f-electron becomes itinerant [14,15]. Non-magnetic La also shows some interesting f-electron effects [16]. Divalent Eu and Yb are like alkaline-earths and are not included here.

As a class the rare earths hydride by adding a new, hydrogen-derived band below the d-levels [4,5], filling tetrahedral interstitial sites. As can be seen from Fig. 1, the driving force is large, and the solubility range small. Up to the approximate composition $MH_{1.8}$ the electrical conductivity rises as much as 40%; yet experimental and theoretical observations indicate that a (small) transfer of charge flows from metal to hydrogen. Since free electronic charge is obviously also being added to the conduction band, this can only be rationalized by considering hydrogen a true (if unusual) metallic addition.

Beyond $MH_{1.8}$ hydrogen begins to enter octahedral as well as tetrahedral sites. Thermodynamically this says that for a given pressure and temperature the heat of formation is not favorable for first filling all tetrahedral sites; in band-structure language it costs too much energy to completely fill the new band this way, and further hydrogens are better accommodated through lowering of existing metal bands. At the same time the lattice begins to shrink, indicating attractive forces are present, i.e., that there are two kinds of hydrogen, bound somewhat differently [17]. In the range from MH_2 to MH_3 a semiconducting

gap begins to develop, until finally the material becomes an insulator, i.e., the hydrogens truly become hydridic. At Nd the M-H distance is reduced to minimum "magic" value of 2.3 Å, characteristic of most electropositive metallic hydrides. The appearance of the hexagonal phase reflects an adjustment to add the extra hydrogen as required by the driving force of the reaction.

Since the f's are for the most part out of the way, the catalytic properties of the lanthanides are reflected mostly by the mobility of the few 5d electrons. This activity peaks at the f^0 (also Ce, possibly involving f's), f^7 and f^{14} stable configurations [18]. The hydriding process itself becomes autocatalytic, as will be discussed below.

Transition Metals

The valence band structure of the transition metals is immediately dominated by the massive d-band; the amount of s-character is small and diffuse, and p-character is not seen until reaching Pd. For the early metals (especially 3d) the d band is broad and the d-electrons are highly involved in metallic bonding. Y and Si behave like rare earths but with a larger range of solubility; Sc is too small to go beyond the dihydride [4].

The tetravalent metals Ti, Zr, and Hf exhibit considerably more complex phase behavior, though they share with the rare-earths, Y and Sc the peculiar increase in electrical conductivity with H-content. Phase diagrams for Ti and Zr are quite different from that for the more electropositive Hf [12], which shows more similarities to the rare earths.

The Group V metals are smaller, less-electropositive, and only the hemi-hydride form easily, the monhydride with more difficulty. An interesting variance in tetrahedral-octahedral site occupation is seen between VH and VD [19]. Hauck [20] has discussed this behavior in terms of electronegativity, and Switendick [5] has carefully analyzed the vanadium system

in terms of electronic structure. Nb and Ta also exhibit properties similar to V, with various compositions, disordered and distorted lattices, etc., but the site occupation seems to remain tetrahedral [21].

The Group VI through VIIIb metals do not form hydrides (Cr can be forced to CrH by electrolytic charging [22]); it simply costs too much energy to force hydrogen into the strongly-bond lattices. Nevertheless, some very interesting electronic effects occur. Even ignoring the oddities introduced by half-filled shell effects, we can see the electronegativity rising to that of hydrogen, signalling a somewhat different kind of alloy chemistry. These metals become endothermic occluders, and coincidentally the phenomenon of activationless dissociation of the H_2 molecule begins to appear. This is in contrast to the more electropositive metals where a fairly large activation energy must be overcome. The result is due to the appearance of relatively-localized antibonding d-levels at the energy for easy dissociation of H_2 , and is part of the total picture of both itinerant and localized d-electron behavior for the latter transition metals.

The culmination of this series is Group VIIc, where for Ni and especially Pd hydrides again can form. Switendick [23] has shown that filled Pd d-states are lowered, with hydrogen electrons filling both empty d-states and the modified s/p states; furthermore, the filling is quite structure-dependent. Actual charge transfer (if any) is quite small, as is predicted from Fig. 1. These states are already full for Pt [23] so a hydride cannot form. NiH can be made by electrolytic charging.

The actinides

The analogy with the transition metals, the actinide f-electrons appear first in broad bands close to the Fermi level, behaving much like

transition metal d's. These electrons dominate the valence band and are responsible for most of the chemical, structural, magnetic and catalytic properties of these metals. The f's become progressively more localized until rare earth properties appear at Am. The major contrast to transition metal behavior lies in the polarized nature of the f-orbitals (like p's) so that optimum bonding configurations often involve exotic, highly-distorted structures. Bond-weakening can occur because of the unfavorable geometry of the f-orbitals; for example, the crystal entropy of Th implies a metal approaching trivalence [24]. The unusual thorium hydrides have been carefully studied [25-27]. Nevertheless there is a discrepancy between UPS and specific heat studies which may involve f-effects.

The Pa and U trihydrides are completely unique in the periodic table. They are stoichiometric yet metallic. Ward et al [28] have discussed UD_3 in terms of a transition metal intermetallic, with two kinds of uranium atoms in the structure; f-f overlap is believed responsible for stabilizing the Al_5 structure. The valence-band XPS spectrum is shown in Fig. 2.

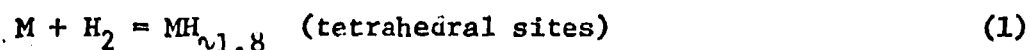
Whereas the neptunium-hydrogen system appears to behave much like the late rare earths [29] there is no contraction in going from NpH_2 to NpH_3 , indicating f-electron effects in the bonding; studies have shown [30] that maximum f-character occurs at Np in the actinide series. The Pu [31,32], Am [33] and presumably later actinide hydrides behave like the late rare earths.

CHEMISORPTION AND CATALYSIS

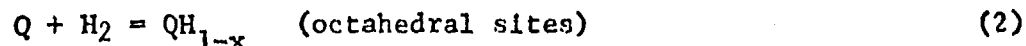
The foregoing discussion considers the addition of hydrogen in forming metallic hydride systems as an alloying process. Switendick [23] has shown that the actual charge transfer is small for either electropositive

or more electronegative metals. Nevertheless, the electronic processes in or near the valence band region can produce large chemical and structural effects. It should be reemphasized that in looking for catalytic properties, the presence of oxide (and/or hydroxide) films, inclusions, grain-boundary impurities, etc., may be of major importance. Indeed, it seems quite probable that hydride initiation (and poisoning) may occur at such sites, rather than directly on the metals. A summary of catalytic properties is given in Table I.

The behavior of electropositive metals and their hydrides can be simply understood in terms of easily ionizable (or shareable) electrons at the Fermi level. An electron-seeking (acidic) contaminant can be strongly chemisorbed. Most atmospheric contaminants are acidic (note the "acid rain" problem that is affecting lakes and rivers). The following hypothetical sequence may serve to illuminate the behavior of most of these systems:



Let us now define $MH_{\sim 1.8} \equiv Q$, where Q is a hypothetical "pseudo-metal" that is actually more metallic than the parent M . From this process we would expect Q to be less electropositive; perhaps, in terms of Fig. 1, like vanadium. We then have:



i.e., the formation of the "monohydride of Q ". The processes of chemisorption at any of the stages in Eqn. 1 or 2 can be quite complex, dealing with a metal (M or Q), a semiconductor or even an insulator. The review paper of Kn8tzing [2] discusses many cases in detail, particularly those of oxygen-bearing gases (CO_2 , SO_2 , CO) on semiconductor surfaces. Dowden [35] considers poisoning in terms of effect on the work function, and points out that the effect of the poison is the largest at the smallest concentrations.

In terms of the availability of electrons for chemisorption, it can be shown [36] that for extremely-pure samples of those metals in which the d- (e.g. Ti, Zr) or f-electrons (e.g., α -U, α -Np, α -Pu) are almost totally involved in metallic bonding, hydriding is very difficult to initiate, even at high temperatures.

As shown earlier, hydrogen dissociates on the late transition metals almost without an energy of activation. A Pd or Ni flashing or coating over a more electropositive metal may provide an immediate source of dissociated hydrogen and therefore rapid attack [37]. Electron-donating molecules can poison this dissociation by giving electronic charge to the metal levels that would be ordinarily available.

A brief comment on the behavior of CO is also appropriate, since the chemisorption of CO on d-metals has produced such a large literature. The picture that emerges is that of a sigma-bonded carbon at the surface in competition with back-bonding (π) surface d-electrons. For the electropositive metals the back-bonding produces dissociation into surface C and O (followed usually by oxidation) [38]. In the middle of the series (e.g. at Fe) dissociation may occur at higher temperatures and non-dissociative adsorption at low temperatures [39]; finally for Ni, Pd, etc., there is only non-dissociative adsorption.

Alloy systems

The remarkable behavior of an electropositive metal upon alloying with various mid-to-late transition metals is of course the matter of prime interest in energy storage. Miedema and co-workers [40,41] have developed systematics based on electronegativity for predicting the heat of formation of transition metal alloys. Watson and Bennett [42,43] have extended this approach in terms of charge transfer and found the surprising result that while net charge transfer as expected is from the more electropositive metal

to the more electronegative one, the d-electron transfer is from the fuller to the emptier bands. Siegel [44] has produced a somewhat similar correlation based on d-band filling.

The hydrogen storage capacity of alloys like FeTi_2 , ZrNi and LaNi_5 must be related to both structural and electronic effects. Not only is there space in the LaNi_5 lattice (9 tetrahedral sites [45]) but there must be newly-derived states to accommodate the hydrogen electrons. XPS spectra for SmCo_5 [46] shows a large d-population at the Fermi level, with clear implication of d-f hybridization. In the analysis of Watson and Bennett [43] a transfer of d-charge to La could be the electronic key to the uptake of six instead of three hydrogens.

In terms of catalysis, LaNi_5 has already been shown to have major catalytic properties [47]. In a recent, excellent paper [48] Wallace et al have clearly delineated both the kinetics and mechanism of hydrogen adsorption. Implicit is surface segregation to form $\text{La}_2\text{O}_3/\text{La}(\text{OH})_3$ and active Ni islands. Here we have apparently the happiest of circumstances, since the hydroxide should be catalytically inert [2], and hydrogen can be dissociated without activation energy on the nickel! Furthermore, as discussed above, Ni will not be affected by acidic contaminants. A similar high activation occurs for Fe [49] in Fe-Ti alloys. It therefore appears that the segregation/oxidation behavior may actually benefit the cycling process in terms of possible contaminants in the system. A truly oxygen and water-free system might exhibit different behavior. Clearly a great deal of interesting surface chemistry remains to be done on these alloy hydride systems in order to provide reliable data on their long-term behavior.

Table I. Summary of Catalytic Behavior of Metallic Hydride Systems

<u>Observation</u>	<u>Electropositive Metals</u>	<u>Electronegative Metals</u>
1. Hydrogen location:	Tetrahedral sites	Octahedral sites
2. Electrical conductivity	Increases upon hydriding	Decreases upon hydriding
3. Activation energy for dissociation:	Appreciable	Nil
4. Poisoned by:	Electrophilic molecules (e.g., SO ₂ , CO ₂ , HCl...)	Electrophobic molecules (e.g., NH ₃ , pyridine...)
5. Hydride:	Is autocatalytic	Poisons reaction [34]

Figure Captions

Fig. 1. Electronegativities of the transition metals, rare earths (RE) and the actinides (AN), in relation to hydrogen.

Fig. 2. Valence-band XPS spectrum for β -UD₃.

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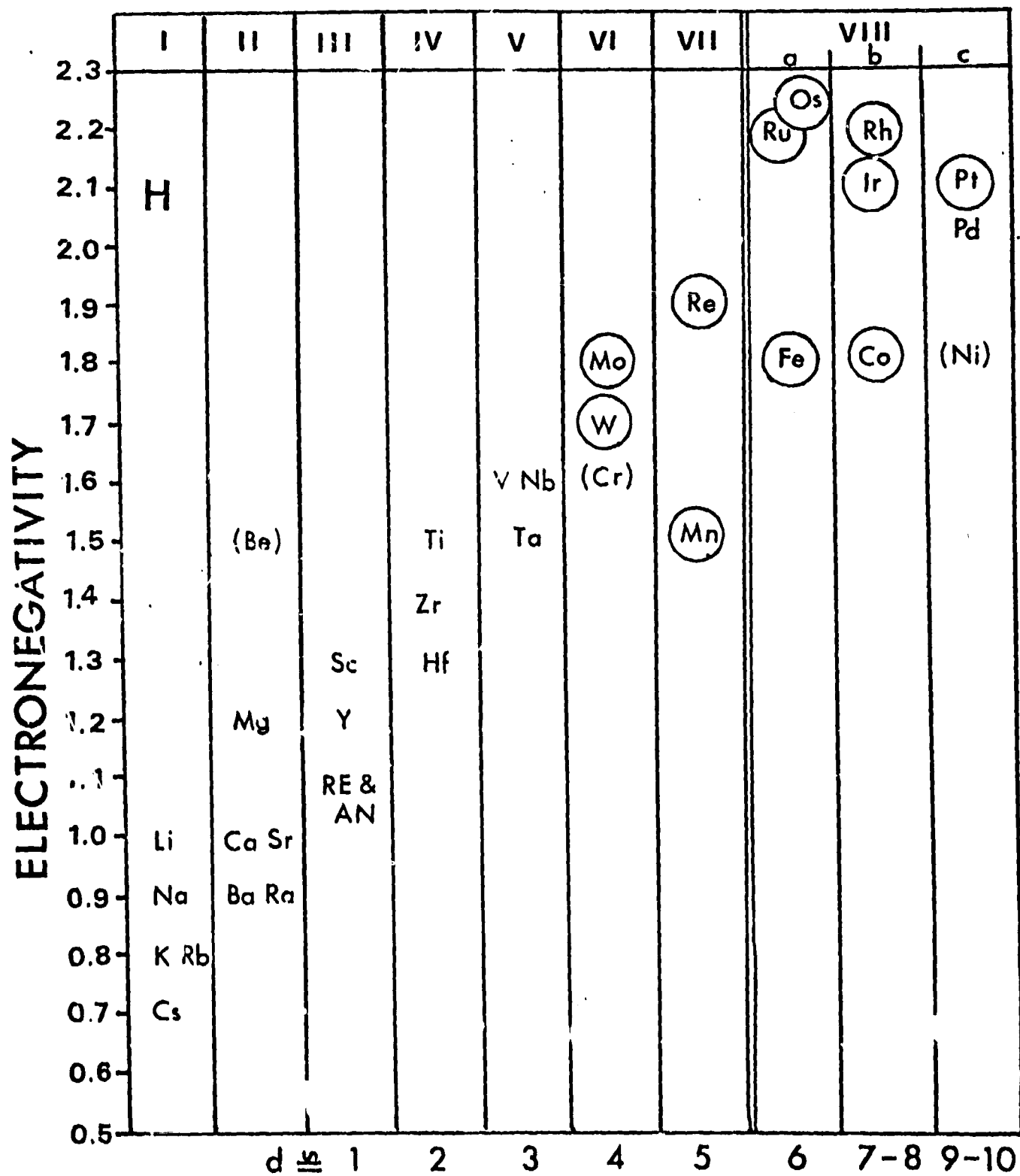


Figure 1.

Figure 2.

